

Mechanism of Enhanced Rectification in Unimolecular Borromean Ring Devices

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We have studied charge transport through individual Borromean Ring complexes, both with and without anchor groups, in gated double barrier tunneling junctions (DBTJs) formed using the electrical breakjunction technique on gold nanowires. While common single molecule device characteristics can be observed with either form of the Borromean Rings, the complexes with anchor groups show strong rectification of conduction in a relatively high percentage of samples. We present our data along with a simple model underlining the mechanism by which the arrangement and composition of the weakly bonding anchor groups attached to the electroactive element may promote a device configuration resulting in rectification.

The field of molecular electronics has grown dramatically in recent years as efforts to explore new limits of device scaling have surged. Diodes represent one of the most basic and essential components of modern electronics, so it is no surprise that a molecular version of the diode has been the focus of many research efforts. There is more than one process by which asymmetrical conduction, i.e. rectification, can occur in metal-molecule-metal assemblies. The most heavily investigated mechanism of molecular rectification is based on the Aviram-Ratner proposal[1], which utilizes a molecule with two insulated molecular orbitals, whose probability amplitudes are asymmetrically oriented with respect to the equilibrium Fermi level of the source and drain electrodes.[2, 3] Another process occurs if the molecule, or the molecular orbital through which current must pass, is situated asymmetrically within the metal-molecule-metal junction.[4] In a breakjunction device, for example, the asymmetrical position of the molecule between the electrodes corresponds to asymmetrical tunneling barriers through which charge must be transported. Because the majority of the applied voltage drops across the larger insulating barrier, the conduction conditions for charge transport through a level are achieved at very different voltages for positive and negative bias. Our experimental observations of rectification through Borromean Ring complexes are based on this mechanism.

The devices we fabricated are composed of a source and a drain electrode plus a conducting substrate that can be used as a back gate. We employed the electrical breakjunction technique first described by Park et al.[5] The molecular compound used as the active element was a Borromean Ring (BR) complex (Figure 1a-c), the synthesis of which was described recently.[6] The control group used bare BR complexes with no anchor groups (or "legs") and the experimental group used BR complexes possessing six anchor groups.

The accumulated data indicates that, like many molecules situated within a breakjunction gap, BR complexes are capable of producing a range of transport properties (including rectification), each of which can be an-

ticipated with a certain frequency of occurrence.[7] The complexes with legs did not result in a greater percentage of devices containing a single molecule. However, the single molecule devices fabricated with the experimental group exhibited device characteristics with more frequent and marked asymmetries, indicating that the property of conduction rectification can be promoted by the addition of anchor groups on this molecular compound. Treating these unimolecular devices as DBTJs, we may invoke the model described by Kornilovitch et al.,[4], which indicates that I-V asymmetries result from the specific arrangement of the metal-molecule-metal junction. We speculate that the general affinity for the complexes of the experimental group to result in a configuration within the breakjunction gap producing such enhanced rectification characteristics is due largely to the arrangement and bonding mode of the six anchor groups that protrude from the BR complex.

The BR complex consists of three interlocking molecular rings, composed of macrocyclic organic ligands interacting with six zinc(II) ions (Fig. 1a-c). The complex was constructed by multiple cooperative self-assembly processes from eighteen original components - six endo-tridentate ligands, six exo-bidentate ligands, and six transition metal ions. These complexes are relatively large (~ 2.3 nm in diameter), making them well suited for use in conjunction with the breakjunction method of fabricating single molecule devices. These complexes are also roughly symmetric in shape. With this relative lack of anisotropy we hope to alleviate inconsistencies that may arise when measuring conductance through its various axes.

The six "legs" on the experimental group of BRs are methyl thioether substituents. The methyl thioethers are coupled to the Schiff base precursor, namely the dialdehyde, by employing a palladium catalyzed Suzuki cross-coupling reaction between the 4-bromo-2, 6-diformylpyridine and 4-methylthiophenyl boronic acid.[8] The anchor groups extend from the body of the BR complex in an octahedrally displaced orientation (Fig. 1d). Among similar research efforts, the prevalent mode of

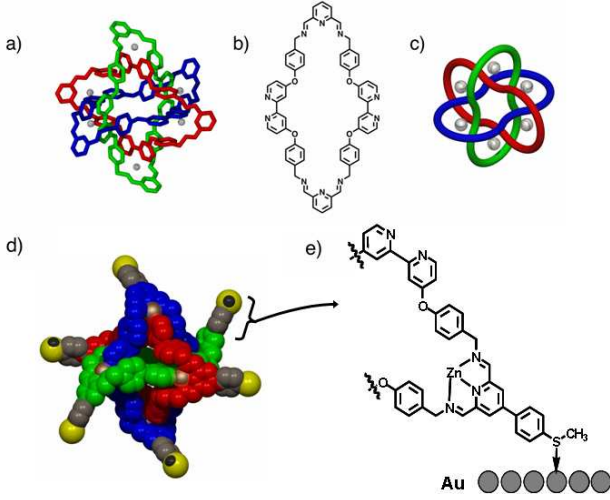


FIG. 1: (Color online) a) The X-ray crystal structure of the zinc(II)-containing Borromean Ring complex. b) The constitution of the macrocyclic ligand, which is repeated three times over in the Borromean Ring complex. c) Graphical representation of the Borromean Ring complex. d) Graphical representation of the complex with anchor groups. e) Chemical structure of anchor group showing dative bonding to a gold atom.

attaching anchor groups to gold electrodes is through covalent bonding.[9, 10, 11] The covalently bound mode is formed from the free thiol, i.e. R-SH. The sulfur atom is negatively charged and the gold is formally positive producing a strong chemical bond. The methyl thioether legs affixed to the BR complex attach to gold in the dative mode of binding (Fig. 1e). An electron pair of the sulfur atom is donated to gold into an empty orbital. Both gold and sulfur are neutral, hence the bond is not as strong as the covalent mode for gold-sulfur.

Fabrication of the DBTJ structures begins with the preparation of arrays of devices on an n+ Si substrate with a 140 Å SiO₂ insulating layer. 1.5 nm of Ti and 13 nm of Au are evaporated onto nanowire patterns defined by electron beam lithography. Bowtie-shaped constriction patterns are produced with minimum widths of less than 100 nm. Additional gold pads for wire-bonding are defined using UV lithography, followed by the deposition of 10 nm Ti and 200 nm Au. The array of samples is cleaned, and a dilute solution of the BR complex (1 mg/2 ml) is deposited onto the devices.[12] The devices are then cooled to 4.2 K, after which the electrical breakjunction technique is used to produce a nanometer-size gap, located at the narrowest portion of the nanowires.

Due to the probabilistic nature of a given sample's specific configuration, a statistical approach is taken to ascertain the device characteristics. Our experimental data was accumulated from the results of approximately 450 samples. After the gap forming process is complete, differential conductance as a function of source-drain voltage is measured for every device. The I-V plots that

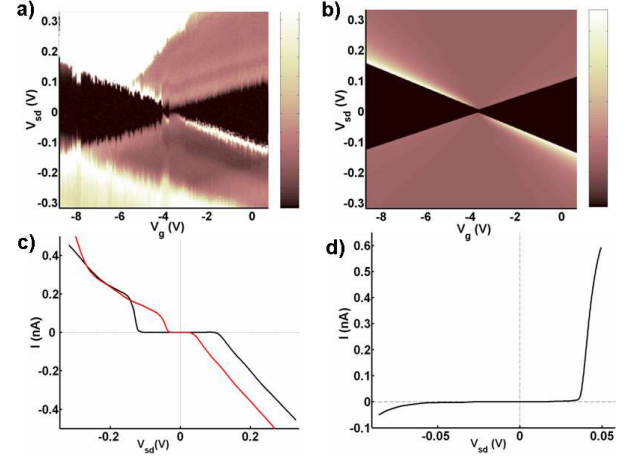


FIG. 2: (Color online) a) Stability diagram of a single molecule transistor utilizing a BR complex. b) Simulation of a gated DBTJ using $C_d \sim C_s$. For (a) and (b) black represents zero conductance and white represents the max conductance (10^{-7} nS). A change in charge state of the BR complex occurs at the critical point, $V_g = V_C$, where the conductance gap goes to zero (~ -3.6 V). c) Two I-V curves from the stability diagram in Fig 2a, obtained by integrating along the traces at $V_g = 0.7$ V (black) and $V_g = -2.3$ V (red). Both I-V plots have rectification ratios of order unity. d) I-V plot of device with rectification ratio of ~ 200 .

result typically fit into one of four categories (detailed by Yu and Natelson[7]), each of which represents a general electrode-molecule configuration within the assembly.

A Breakjunction device with a moderately sized gap in which a single molecule or complex is present (i.e. a metal-molecule-metal configuration) will have an I-V plot exhibiting a blocked region around $V_{sd} = 0$ with strong nonlinearity outside this region. Conduction occurs as electrons sequentially tunnel from one electrode onto the active element and then onto the second electrode, as established in the seminal works on the subject.[13, 14] This can also be confirmed by computer simulation. Fig 2a shows an experimentally obtained stability diagram (or colormap) measuring differential conductance ($\partial I / \partial V$) as a function of both source-drain bias (V_{sd}) and gate voltage (V_g). Treating the tunneling barriers as though comprised of a capacitive and a resistive element, our computer model of electrons sequentially tunneling through a DBTJ can project a theoretical stability diagram with nearly identical ground state properties as those found in the experimental data set (Fig 2b). The positive and negative slopes of the blocked region (tunneling thresholds) are determined by the ratios C_g/C_d and C_g/C_s , respectively[15] (C_g , C_d , and C_s are the capacitances between the molecule-gate, molecule-drain, and molecule-source electrodes). The relative slopes of the tunneling thresholds in Fig 2a indicate that the BR complex is almost equally coupled to the source and drain electrodes, and non-rectifying I-V plots result (Fig 2c). We contend that highly asymmetric I-V plots, as in Fig

2d, result when the electroactive element has a stronger coupling to either the source or drain electrode.

A device qualified as a “rectifier” if it possessed a rectification ratio greater than 20. Of the BR samples without anchor groups, 37% were confirmed to consist of a metal-molecule-metal configuration. Of these “working” single molecule devices, 3% had rectification ratios > 20 . For the BR samples with anchor groups there was a 35% chance of a device resulting in a metal-molecule-metal configuration, but of these devices over 15% had rectification ratios > 20 . Furthermore, only one device among the control group had a rectification ratio > 50 . Among the devices fabricated using the BR complex with methyl thioether anchor groups, half of the rectifying samples had rectification ratios > 100 .

The single molecule assembly consists of five parts: a source and drain electrode, the central complex through which electrons must pass, and two insulating barriers (Fig. 3a,b). The tunneling barriers are established by the physical separation between the complex and an electrode and/or the strength of the bond between an electrode and one or more anchor groups of the BR complex. The rectification properties of the assembly are primarily dictated by three parameters: the energy difference between the equilibrium Fermi level of the electrodes and the nearest molecular orbital level, Δ (HOMO level[16, 17]), and the coupling strengths of the molecule-source and molecule-drain tunneling barriers, Γ_s and Γ_d . The voltage drops across the barriers are proportional to their respective coupling strengths. The ratio of the voltage drops on the opposing barriers, η , is $\sim \Gamma_s/\Gamma_d$.

The mechanism of rectification follows from Kornilovitch et al.[4] The “turn on” voltages for the forward and reverse directions are

$$V_R = (1 + \eta) \frac{\Delta}{e}, \quad V_F = \left(\frac{1 + \eta}{\eta} \right) \frac{\Delta}{e} \quad (1)$$

The ratio of the forward and reverse turn-on voltages is $V_R/V_F = \eta$. For any η greater than 1, there is a voltage window $V_F < |V| < V_R$ within which there is significant conduction in the forward direction, but little or no conduction in the reverse direction (Fig 3c-d). As the difference in coupling strength between opposing sides of the complex grows, η becomes larger and hence, the difference between the two threshold voltages increases.

Fig 3f shows another simulation using nearly identical parameters as those used to produce Fig 2b with the exception that C_d has been increased and C_s has been reduced to represent a shift in position (or coupling strength) of the complex toward the drain electrode. The reduced slope of the tunneling threshold for $V_{sd}, V_g > 0$, indicates that a relatively large change in gate bias causes little change in the position of the forward “turn on” voltage, V_F . Unlike the two curves in Fig 2c, the I-V measurements in Fig 3g undergo a more modest transformation as the gate bias is shifted, which is in

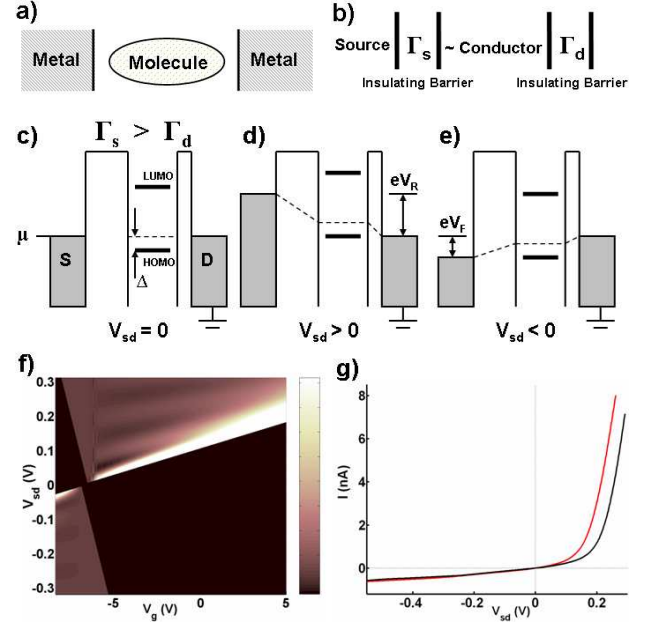


FIG. 3: (Color online) a) Basic molecule-electrode configuration. b) The five components of a single molecule assembly. c) Energy level diagram of electrodes and BR complex for $V_{sd} = 0$. d) For positive bias (forward voltage direction), the current will increase when the HOMO level of the complex aligns with the Fermi level of the source electrode. e) For negative bias (reverse voltage direction), the current will increase when the HOMO level of the complex aligns with the Fermi level of the drain electrode. A voltage must be applied such that the energy of the HOMO level goes up by Δ . The majority of the voltage drop occurs over the drain-molecule tunneling barrier. This causes $V_F > V_R$. f) Simulation using same parameters as Fig 2b, except $C_d > C_s$. V_g offset due to background charge. Max $\partial I/\partial V = 10^{-6}$ nS g) Measured I-V traces with rectification ratio of ~ 25 , taken at $V_g = 0$ V (red) and $V_g = 3$ V (black). The rectification is less pronounced compared to Fig 2d, but the current density is an order of magnitude greater before breakdown.

agreement with our simulation (V_C and V_R cannot be observed due to the onset of significant instability leading to electrostatic breakdown). Hence rectification can derive from the molecule-electrode configuration, and like typical single molecule transistor characteristics, results from a single particle sequential tunneling mechanism.

Compromising factors, however, limit the effectiveness of these rectifiers. If the bulk of the BR complex is too close to one electrode, or it is too strongly coupled, the conducting level widens such that the transmission probability will be significant for all energies, and there will be little difference between the currents in the forward and reverse directions. Conversely, the larger of the two tunneling barriers controls the overall amplitude of the current as well as the size of the rectification window. As the width of this barrier is increased, the rectification ratio increases linearly while the current decays exponentially.

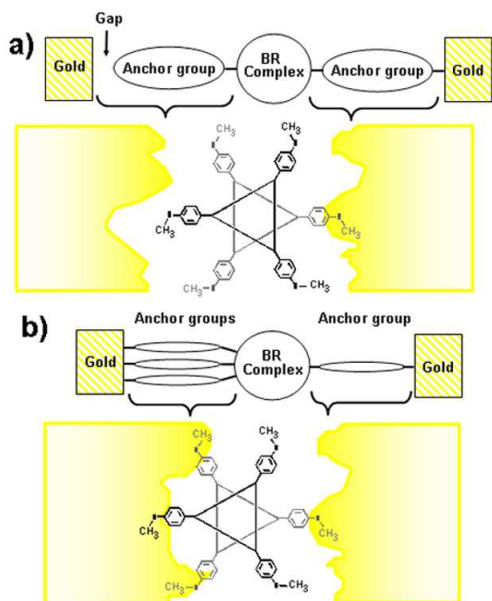


FIG. 4: (Color online) Two possible electrode-molecule configurations resulting in conduction rectification. a) The complex is chemically bonded to only one electrode. b) The complex is attached to opposing electrodes through an unequal number of bonds. The asymmetry has no preferential orientation (i.e. either tunneling barrier can be the larger). The black and gray triangles represent the two facial planes of the octahedral complex.

Compared to the control complexes with no legs, the Borromean Ring complexes with methyl thioethers anchor groups resulted in an equal percentage of devices with an electrode-(single molecule)-electrode configuration, but five times the percentage of devices with strong rectification. Thus the addition of anchor groups on the BR complex promotes rectification, which we ascertain to result from molecule-electrode configurational asymmetries. The means by which the anchor groups force this configurational asymmetry is a matter of speculation. The methyl thioethers legs have a weak affinity for gold, providing some level of stability, but the chances of both source and drain ends forming chemical bonds is reduced since the mode of binding is less favored compared to the covalent bonding mode. This weaker dative bonding mode implies that more assemblies may have one side bonded and the other side free (Fig. 4a), leading to strongly asymmetric tunneling barriers.

Rectification may also be encouraged via the geometry of the anchor groups. The radially protruding anchor groups may act like bumper guards to stop the complex from positioning itself so close to an electrode that the energy levels are overly broadened. Also, because there are six anchor groups, three on each of the two tripodal facial planes, configurations may occur in which the source and drain electrodes are connected to the complex through an unequal number of bonds, again resulting in asymmetrical tunneling barriers (Fig 4b).

Conduction asymmetries due to unequal coupling to the electrodes or to an asymmetric central molecular unit have been observed in the past but, current rectification ratios in these studies were of order unity, making them unsuitable for practical applications.[10] The addition of anchor groups on the BR complex play a pivotal role in the resulting molecule-electrode configuration, specifically in promoting configurations with strongly asymmetric tunneling barriers. We postulate that the geometry and bonding mechanism of the anchor groups on the BR complexes precipitate this outcome. Affecting the preferential configuration of a molecule within a breakjunction represents a significant step toward a more complete understanding of physics on the molecular level and ultimately extends our ability to exert further control over such nanoscale systems.

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